Computing rovibrational levels of polyatomic molecules with curvilinear internal vibrational coordinates and an Eckart frame

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Variational methods to compute rovibrational levels: normal coordinates

- For molecules with small-amplitude motion, normal coordinates and an Eckart frame are very efficient : Watson kinetic energy operator (KEO)

$$T = -\frac{1}{2}\sum_{k}\frac{\partial^2}{\partial Q_k^2} + \frac{1}{2}\sum_{\alpha\beta}\left(J_\alpha - \pi_\alpha\right)\mu_{\alpha\beta}\left(J_\beta - \pi_\beta\right) - \frac{1}{8}\sum_{\alpha}\mu_{\alpha\alpha}$$

$$\text{Eckart condition :} \quad \sum_{i=1}^{N} m_i \mathbf{a}_i \times \mathbf{r_i} = 0$$

1. J. K. G. Watson, *Mol. Phys.*, 15, 479(1968)
2. C. Eckart, *Phys. Rev.*, 47, 552(1935)

- Normal coordinate variational calculations on CH_4
  - J = 0 : S. Carter, H. M. Shnider, and J. M. Bowman, JCP 110, 8417 (1999)

    E. Matyus, G. Czako, B. T. Sutcliffe, and A. G. Csaszar, JCP. 127, 084102 (2007).
  - J > 0 : J. Wu, X. Huang, S. Carter, and J. M. Bowman, CPL 426, 285 (2006).

    M. Rey, A. V. Nikitin and V. G. Tyutereva, PCCP, 15, 10049 (2013)

Variational methods to compute rovibrational levels: internal coordinates

- For molecules with large-amplitude motion(LAM), internal coordinates are necessary: better representation of potential.
- But internal coordinates are *always* used with a **simple geometrical frame**: bond-z, bisector etc for 3-atom, 4-atom, 5-atom molecules
  - For example, our first rovibrational calculation of CH_4 in 2004

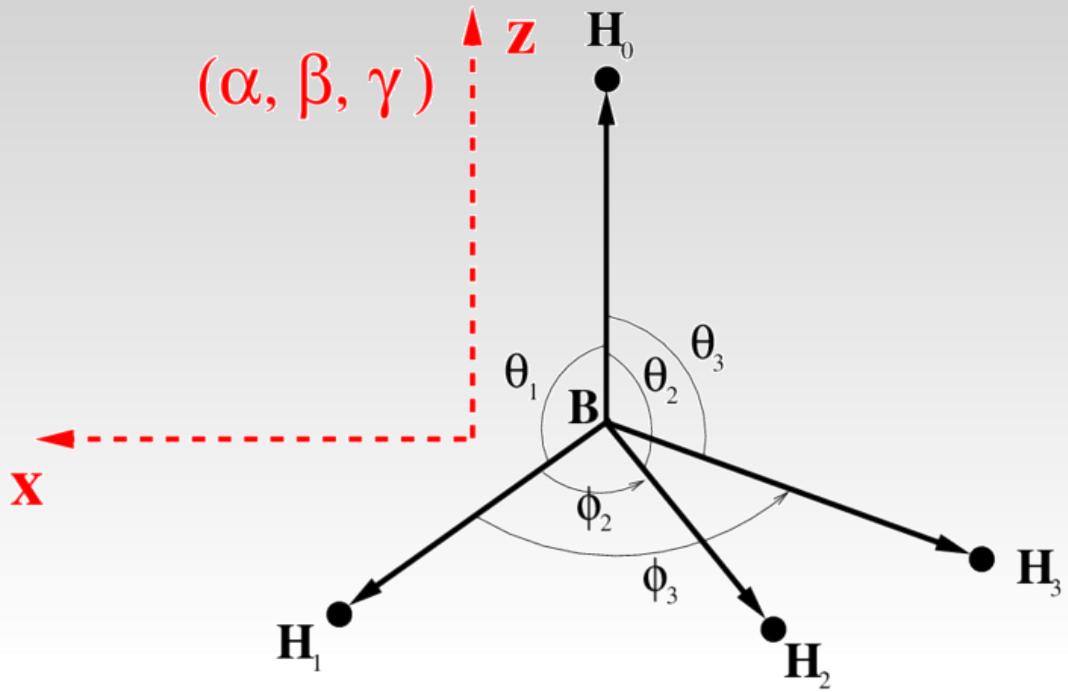
X.-G. Wang and T. Carrington, *J. Chem. Phys.*, 121, 2937(2004)

- Internal coordinates and Eckart frame (This talk)

X.-G. Wang and T. Carrington, *J. Chem. Phys.*, 138, 104106(2013)

A bond-z frame for CH_4: defined by two vectors

- Why bond-z frame?
- Simple analytical KEO
- Simple kinetic matrix elements in spherical harmonics basis



$$g_{\alpha_0}(r_{\alpha 0})g_{\alpha_1}(r_{\alpha 1})g_{\alpha_2}(r_{\alpha 2})g_{\alpha_3}(r_{\alpha 3})\Theta_{l_1}^{m_1}(\theta_1)Y_{l_2}^{m_2}(\theta_2,\phi_2)Y_{l_3}^{m_3}(\theta_3,\phi_3)|JK\rangle$$
with $m_1 = K - m_2 - m_3$

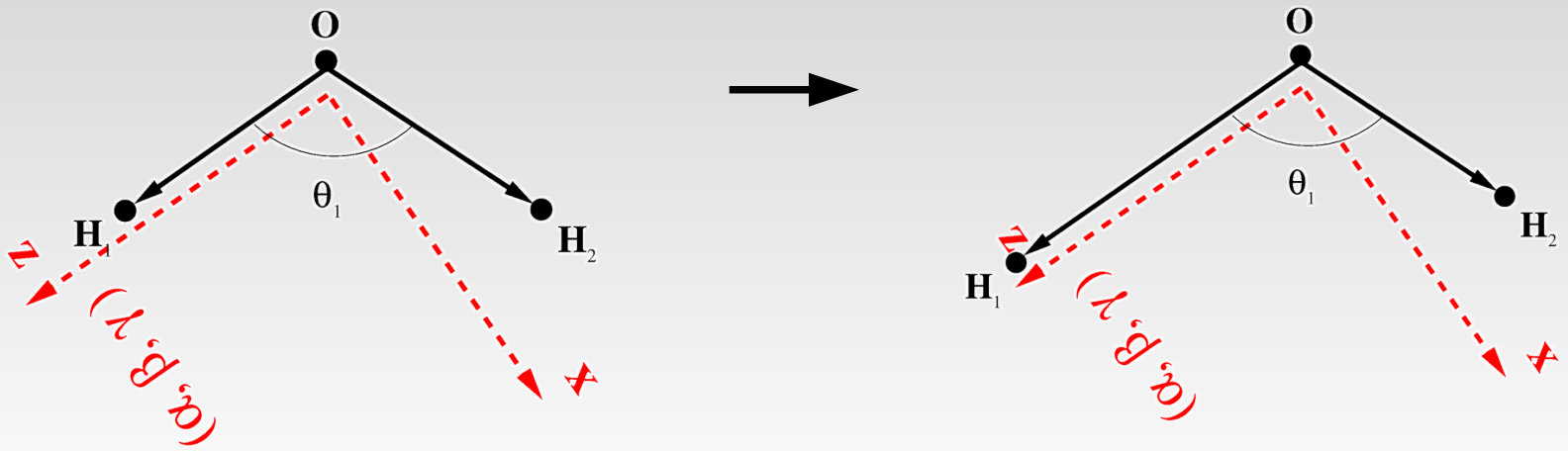
- Contract this basis for each K to get smaller basis $|s(r)b(\theta)^K\rangle|JK\rangle$
  - very costly to do this for each K

Method is best for LAM molecules
Limited to small J due to coupling

1. X.-G. Wang and T. Carrington, *J. Chem. Phys.*, 119, 101(2003) ($J = 0$)
2. X.-G. Wang and T. Carrington, *J. Chem. Phys.*, 121, 2937(2004) ($J = 1$)

Compare bond-z frame with Eckart frame

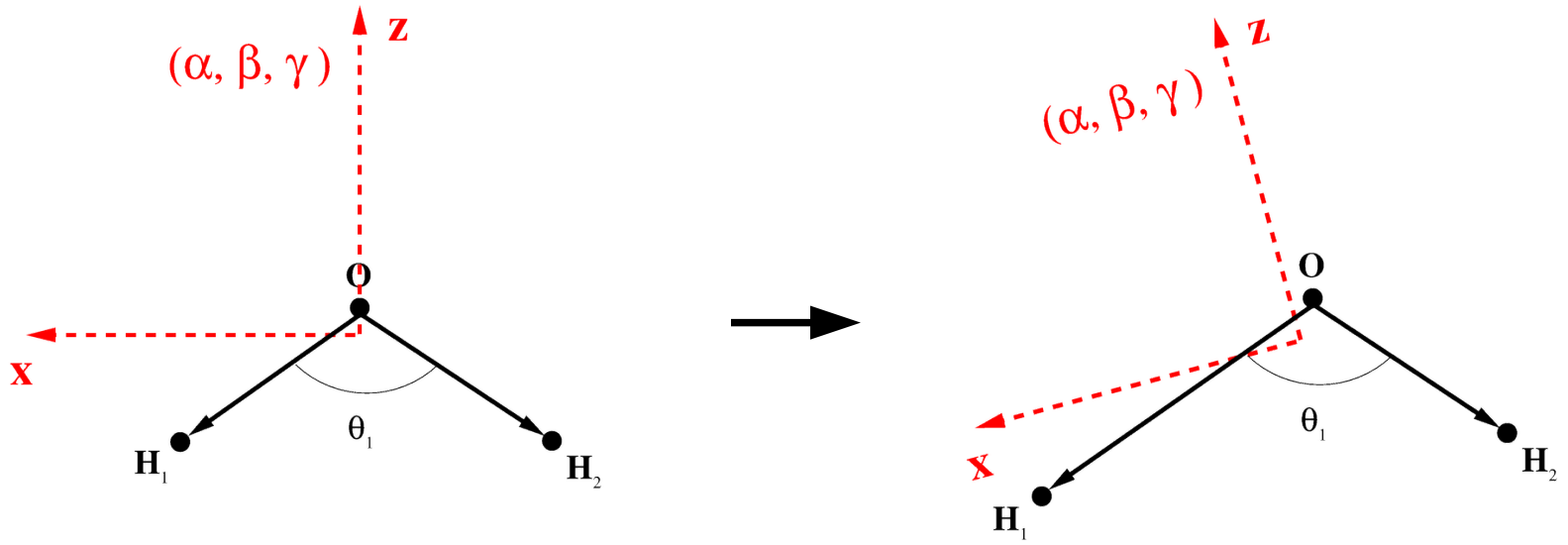
- When one bond is stretched, **bond-z** frame does not react. No rotation.



- Geomtrical frame has large Coriolis couplings, e.g. bond-z frame for CH_4

$$T_{\mathrm{Cor}} = -2B(r_0)(l_{2x}J_x + l_{2y}J_y) \text{ with } B(r_0) = 14.1 \text{ cm}^{-1}$$

- When one bond is stretched, **Eckart** frame thinks the molecule is rotated



Internal coordinate Eckart frame KEO notoriously complicated

- Why nobody uses it before? Because the Eckart KEO is very complicated.
- Analytical KEO is only derived for H_2O and planar 4-atom molecules
- Radau coordinate Eckart frame KEO for H_2O:

H. Wei and T. Carrington, Chem. Phys. Lett. **287**, 289-300 (1998)

$$T = T^{\text{vib}} + T^{\text{rot}} + T^{\text{cor}},$$

where

$$\begin{aligned}
T^{\text{vib}} &= -\frac{1}{2m_1}\frac{\partial^2}{\partial R_1^2} - \frac{1}{2m_2}\frac{\partial^2}{\partial R_2^2} \\
&- \left(\frac{1}{2m_1 R_1^2} + \frac{1}{2m_2 R_2^2}\right)\frac{\partial}{\partial c}(1-c^2)\frac{\partial}{\partial c}, \\
T^{\text{rot}} &= \frac{1}{2}[G_{xx}J_x^2 + G_{yy}J_y^2 + G_{zz}J_z^2 + G_{xy}(J_xJ_y + J_yJ_x)], \\
T^{\text{cor}} &= -\frac{i}{2}\sum_{v=R_1,R_2,c}\left[G_{vz}\frac{\partial}{\partial v} + \frac{\partial}{\partial v}G_{vz}\right]J_z,
\end{aligned}$$

1. H. Wei and T. Carrington, *J. Chem. Phys.*, 107, 9493(1997) (bond coordinate)
2. H. Wei, *J. Chem. Phys.*, 118, 7208(2003) (planar 4-atom molecules)

Analytical Radau coordinate Eckart frame KEO for H_2O

$$
\begin{aligned}
G_{R_1 z} &= -\Lambda\epsilon\rho R_2 \sin(\theta-\theta_e),\\
G_{R_2 z} &= \Lambda\rho R_1 \sin(\theta-\theta_e),\\
G_{cz} &= \Lambda \sin\theta[1-\epsilon\rho^2-\rho(R_1/R_2-\epsilon R_2/R_1)\cos(\theta-\theta_e)],\\
G_{xx} &= \Lambda(1-c^2)^{-1}[S_1^2+S_2^2/\epsilon],\\
G_{yy} &= \Lambda(1-c^2)^{-1}[C_1^2+C_2^2/\epsilon],\\
G_{xy} &= \Lambda(1-c^2)^{-1}[-S_1C_1+S_2C_2/\epsilon],\\
G_{zz} &= \Lambda[1+\epsilon\rho^2],
\end{aligned}
$$

where

$$
\begin{aligned}
S_1 &= \sin(\theta-\eta_e)+\epsilon\rho(R_2/R_1)\sin(\theta_e-\eta_e),\\
C_1 &= \cos(\theta-\eta_e)+\epsilon\rho(R_2/R_1)\cos(\theta_e-\eta_e),\\
S_2 &= \epsilon\rho\sin(\theta-\theta_e+\eta_e)+(R_1/R_2)\sin\eta_e,\\
C_2 &= \epsilon\rho\cos(\theta-\theta_e+\eta_e)+(R_1/R_2)\cos\eta_e,\\
1/\Lambda &= m_1[R_1^2+(\epsilon\rho R_2)^2+2\epsilon\rho R_1R_2\cos(\theta-\theta_e)],
\end{aligned}
$$

- Difficult to use
- Almost impossible to derive for a larger molecule
- The solution is to use numerical Eckart KEO

Internal coordinate KEO for any frame

- For *any molecule-fixed frame*, the classical kinetic energy is

$$T_{class} = \frac{1}{2}(\mathbf{P}^t \ \mathbf{J}^t) \begin{pmatrix} \mathbf{G_{vv}} & \mathbf{G_{rv}} \\ \mathbf{G_{rv}^t} & \mathbf{G_{rr}} \end{pmatrix} \begin{pmatrix} \mathbf{P} \\ \mathbf{J} \end{pmatrix}$$

  - $\mathbf{G}_{vv}$ is the Wilson G-matrix

- Its quantum mechanical form (Meyer and Gunthard 1968, Pickett 1972)

$$T_{QM} = \left(\frac{1}{2}\mathbf{P^t G_{vv} P} + V'\right) + \frac{1}{2}\mathbf{P^t G_{rv} J} + \frac{1}{2}\mathbf{J^t G_{rv} P} + \frac{1}{2}\mathbf{J^t G_{rr} J}$$

where

$$P_k = -i\frac{\partial}{\partial r} \qquad \text{for } k = r$$

$$P_k = -i\left(\frac{\partial}{\partial \theta} + \frac{1}{2}\cot\theta\right) \qquad \text{for } k = \theta$$

$$P_k = -i\frac{\partial}{\partial \phi} \qquad \text{for } k = \phi$$

  - The modified P_k for θ is due to volume element $\sin\theta$ (this work)
  - We use a different analytical T_{vib} to compute vibrational wavefunctions.

How does one compute G_{rv} and G_{rr} in an Eckart frame?

- Numerical Eckart KEO was used in high order perturbative calculation of $J > 0$ levels
  - A. B. McCoy, D.C. Burleigh and E. L. Sibert, *JCP* (1991) for H_2CO $J > 0$ levels
  - X.-G. Wang and E. L. Sibert. *Spectrochim. Acta A* (2002) for CH_4 $J > 0$ levels

$$\mathbf{G_{rv}} = -\mathbf{C}\mathbf{G_{vv}}$$

$$\mathbf{G_{rr}} = \mu + \mathbf{C}\mathbf{G_{vv}}\mathbf{C^t} \quad \text{with } \mathbf{C} = \mu\mathbf{X}$$

$$X_{\alpha,k} = \sum_{i=1}^{N} m_i \epsilon_{\alpha\beta\gamma} x_{\beta i} \frac{\partial x_{\gamma i}}{\partial Q_k}$$

- **X** is calculated from the inverse of **B** matrix

$$B_{k,\alpha i} = \frac{\partial Q_k}{\partial x_{\alpha i}}$$

- **B** is a 3N x 3N matrix obtained by augmenting Q_k (internal coord.) with 6 rows
- 3 rows are chosen to satisfy the Eckart condition (or **condition for any frame**).
- **B** is computed with finite difference.

For H_2O numerical and analytical KEO agree well

Radau coordinates at $r_1 = 1.7$ bohr , $r_2 = 1.5$ bohr , $\theta = 100^\circ$

gv(1,1)	4×10^{-14}
gv(1,2)	$< 10^{-14}$
gv(1,3)	$< 10^{-14}$
gv(3,3)	2×10^{-13}
grv(2,1)	$< 10^{-14}$
grv(2,2)	1×10^{-14}
grv(2,3)	$< 10^{-14}$
grr(1,1)	$< 10^{-14}$
grr(3,3)	1×10^{-14}
grr(1,3)	$< 10^{-14}$
grr(2,2)	$< 10^{-14}$

How to use the numerical Eckart KEO?

- Use $|v\rangle|JK\rangle$ as basis (vibration basis is independent of K)

- First, solve the vibrational wavefunctions with contracted stretch and bend basis (Wang and Carrington 2003),

$$|sb\rangle \longrightarrow |v\rangle$$

- Compute and store two types of integrals in basis $|v\rangle$
  - For G_{rr} terms

Use F-matrix idea to store

$$\langle v'|G_{\alpha,\beta}|v\rangle = \sum_{s',b'}\sum_{s,b}\langle v'|s'b'\rangle\langle s'b'|G_{\alpha,\beta}|sb\rangle\langle sb|v\rangle$$

  - For G_{rv} terms
    - If k is a stretch

$$\langle v'|\sum_k G_{\alpha,k}P_k|v\rangle = \sum_k\sum_{s',b'}\sum_{s,b}\sum_{s''}\langle v'|s'b'\rangle\langle s'b'|G_{\alpha,k}|s''b\rangle\langle s''|P_k|s\rangle\langle sb|v\rangle$$

    - If k is a bend

$$\langle v'|\sum_k G_{\alpha,k}P_k|v\rangle = \sum_k\sum_{s',b'}\sum_{s,b}\sum_{b''}\langle v'|s'b'\rangle\langle s'b'|G_{\alpha,k}|sb''\rangle\langle b''|P_k|b\rangle\langle sb|v\rangle$$

ΔV matrix : *F*-matrix method

We do not store the ΔV matrix, but store the F-matrix. $|\alpha\rangle$ is the DVR basis

$$\langle s'b'|\Delta V(r,\theta)|sb\rangle = \sum_{\alpha}\langle s'|\alpha\rangle \boxed{\langle \alpha b'|\Delta V(r_\alpha,\theta)|\alpha b\rangle} \langle\alpha|s\rangle$$

$$\boxed{F^{(\alpha)}_{b'b}}$$

- Distribute α over hundreds of processors when computing the F-matrix.
- 100% parallelization efficiency

	α	α'	α''	$\cdots$
α	$F^{\alpha}_{b'b}$	0	0	0
α'	0	$F^{\alpha'}_{b'b}$	0	0
α''	0	0	$F^{\alpha''}_{b'b}$	0
$\vdots$	0	0	0	$\ddots$

$= \langle \alpha' b'|\Delta V|\alpha b\rangle$

3-index array: F-matrix

X.-G. Wang and T. Carrington, *J. Chem. Phys.*, 119, 101(2003)

For CH_4, 33 G elements to integrate (15 even G and 18 odd G)

- 6 G_{rr} terms,

$$\begin{pmatrix} G_{xx} & G_{xy} & G_{xz} \\ & G_{yy} & G_{yz} \\ & & G_{zz} \end{pmatrix} = \begin{pmatrix} e & o & e \\ & e & o \\ & & e \end{pmatrix}$$

- 27 G_{rv} terms.

$$\begin{pmatrix} G_{x,r_1} & G_{x,r_2} & G_{x,r_3} & G_{x,r_0} & G_{x,\theta_1} & G_{x,\theta_2} & G_{x,\theta_3} & G_{x,\phi_2} & G_{x,\phi_3} \\ G_{y,r_1} & G_{y,r_2} & G_{y,r_3} & G_{y,r_0} & G_{y,\theta_1} & G_{y,\theta_2} & G_{y,\theta_3} & G_{y,\phi_2} & G_{y,\phi_3} \\ G_{z,r_1} & G_{z,r_2} & G_{z,r_3} & G_{z,r_0} & G_{z,\theta_1} & G_{z,\theta_2} & G_{z,\theta_3} & G_{z,\phi_2} & G_{z,\phi_3} \end{pmatrix}$$

$$= \begin{pmatrix} o & o & o & o & o & o & o & e & e \\ e & e & e & e & e & e & e & o & o \\ o & o & o & o & o & o & o & e & e \end{pmatrix}$$

- Need to integrate these G elements in basis $|sb\rangle$, the F-matrix idea
  - New concept :**Wilson G-matrix surface** is like potential energy surface
  - We have 33 Wilson G-matrix surfaces, 33 times more work.
- All this work is parallelizable. Computing these integrals take 24 hours with 192 cores and 0.5 TB disk. It is only done once. The final stored matrices $\langle v'|G_{\alpha,\beta}|v\rangle$ and $\langle v'|\sum_k G_{\alpha,k}P_k|v\rangle$ are very small.

Basis for J = 0 calculation

Table 1: $J = 0$ basis sets.

	Bend basis	Stretch basis	$\rightarrow$	full-d basis	Ref.
Primitive basis	6.67×10^6	10^4	$\rightarrow$	6.67×10^{10}	
Contracted basis b0s1	280	260	$\rightarrow$	72,800	Wang and Carrington, JCP(2003)
Contracted basis b3s1	954	260	$\rightarrow$	248,040	This work, used for $J > 0$
Contracted basis b4s1	1242	260	$\rightarrow$	322,920	This work

- The current basis with $N_b = 1242$ is almost 5 times larger than our basis in 2003
- Diagonlization of a matrix of size 323,000 is done with Lanczos algorithm (the matrix has a product structure)
- The contracted J = 0 basis is larger than those used in normal coordinate approach. So we have the best converged vibrational levels and wavefunctions

Quality of vibrational levels

Table 1: The error of selected vibrational levels calculated with different bend basis sets.

Assign	Basis b3s1 $N_b = 954$ $E_b^{\rm cut}$=10140. cm^{-1}	Basis b4s1 $N_b = 1242$ $E_b^{\rm cut}$=12000. cm^{-1}
P=4		
(00)(04) A1	0.00	5128.03
...	...	...
(00)(40) E	0.01	6118.41
(00)(40) E	0.01	6124.00
P=5		
(00)(05) F2	0.07	6385.84
(00)(05) A1	0.06	6413.47
...	...	...
(01)(30) F2	0.01	7578.18
P=6		
(00)(06) A1	0.19	7615.70
(00)(50) F2	0.20	7631.85
(00)(50) E	0.01	7639.04

Chosen for this work

- Quality : the vibrational levels have small errors up to 7500 cm^{-1} (about P = 5)
- |v> basis is of high quality

Basis for J>0 calculation

Table 1: $J > 0$ basis sets

	$N_b \times N_s$	$\rightarrow$	N_{vib}	$E_v^{\rm cut}$ $(\rm cm^{-1})$
Basis b3s1P2	954×260	$\rightarrow$	25	3100.
Basis b3s1P3	954×260	$\rightarrow$	80	4600.
Basis b3s1P4	954×260	$\rightarrow$	220	6200.
Basis b3s1P5	954×260	$\rightarrow$	551	7800.
Basis b3s1P6	954×260	$\rightarrow$	1210	9100.
Basis b3s1P6x	954×260	$\rightarrow$	1939	10000.
Basis b3s1P7	954×260	$\rightarrow$	2949	11000.

Largest used in this work

- Basically we truncate vibrational basis sets by the polyad

- Rotational levels up to P = 4 could be converged with basis P = 5
  - It of course depends on how high J one wants
- The large basis uses about 3000 vibrational functions.

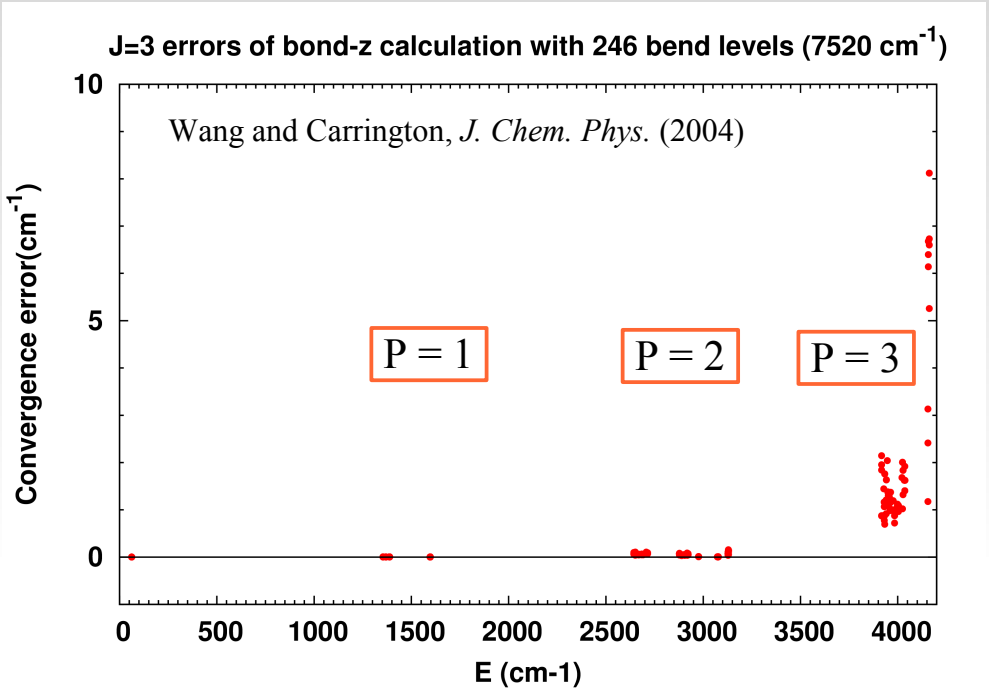
Table 1: $J = 1$: convergence and comparison with previous calculations. $N_b = 437$

$P=2$ $N_{vib}=25$ $E_v^{\rm cut}$=3100. $\rm cm^{-1}$	$P=3$ $N_{vib}=80$ $E_v^{\rm cut}$=4600. $\rm cm^{-1}$	$P=4$ $N_{vib}=220$ $E_v^{\rm cut}$=6200. $\rm cm^{-1}$	$P=5$ $N_{vib}=551$ $E_v^{\rm cut}$=7800. $\rm cm^{-1}$	Theory WC2004	Expt. Albert2009	
.014	.001	.001	10.429	10.43	10.48 (F1)	
.022	.022	.000	1312.410	1312.41	1311.43 (A2)	
.014	.014	.000	1317.250	1317.25	1316.30 (F2)	
.020	.018	.000	1326.727	1326.73	1325.82 (F1)	
.019	.018	.000	1327.030	1327.03	1326.13 (E)	
.015	.014	.000	1543.788	1543.79	1543.93 (F2)	
.017	.017	.000	1543.910	1543.91	1544.05 (F1)	
.122	.025	.023	2600.011	2600.02	2597.37 (F1)	P=2 starts
...	...	...	...	...	...	
.131	.020	.018	3075.813	3075.82	3076.01 (F1)	P=2 ends
N.A.	.293	.006	3875.859	3875.95	3871.56 (A2)	P=3 starts
N.A.	...	...	...	...	...	
N.A.	.160	.002	4606.426	4606.50	4606.55 (F1)	P=3 ends

75 basis functions for 75 states!

- Good convergence with $N_{\rm vib}$. About 100-200 vibrational functions are enough for $J = 1$.
- Good agreement with our previous calculations Wang and Carrington, JCP(2004)

Compare bond-z frame calculations with Ecarkt-frame calculations

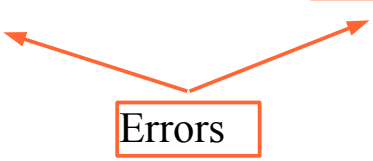


Bond-z frame calculations

- Errors are relative to the converged Eckart frame calculations
- $J = 3$ numbers were not published in Wang and Carrington, *J. Chem. Phys.*, (2004) because we could not converge levels of $P \geq 3$

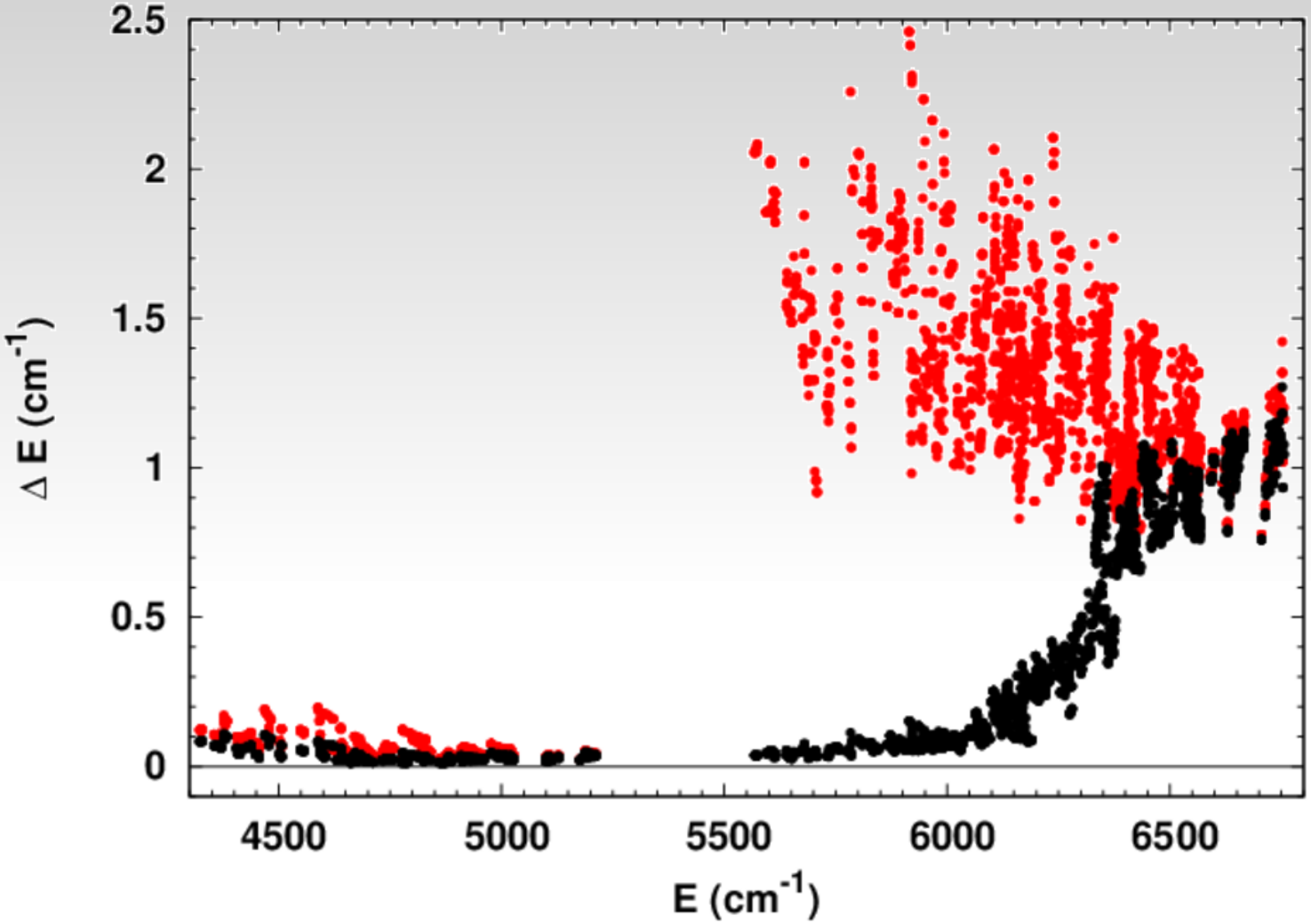
Table 1: $J = 10$ lowest and highest Octad levels, lowest and highest Tetradecad levels, and lowest Icosad levels of CH_4. The first two columns are errors wrt column 3.

$N_{vib} = 1210$	$N_{vib} = 1939$	$N_{vib} = 2949$
P=3, Octad		
0.12	0.08	4322.89 (F2)
0.12	0.08	4323.66 (E)
...	...	...
0.04	0.04	5211.71 (E)
0.04	0.03	5211.74 (F2)
P=4, Tetradecad		
2.05	0.04	5568.11 (A)
2.05	0.04	5568.77 (F)
2.06	0.04	5569.54 (F)
...	...	
1.20	1.08	6755.08 (E)
1.16	1.05	6755.26 (F)
P=5, Icosad		
2.92	2.40	6810.87
2.96	2.41	6811.19
3.06	2.44	6814.01



- With 2949 vibrational functions, $J = 10$ levels of Tetradecad converged to within 1 cm^{-1}.

The convergence of J = 10 tetradecad levels



- Red $N_{vib} = 1210$
- Black $N_{vib} = 1939$
- Benchmark $N_{vib} = 2949$

Conclusions

- A method using internal coordinate (Radau) and Eckart frame is developed to calculate rovibrational levels:
  - Contracted stretch and bend functions used to compute vibrational wavefunctions
  - Numerical Eckart KEO
- We (finally) can compute converged high-J (J = 10) levels of highly excited vibrational states (Tetradecad) for methane
- A better methane potential is urgently needed.
- The method's best molecule is not methane, but LAM molecules: ketene, $C_2H_3^+$, $H_3O_2^-$ etc
- The method can be used for other frames

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